

# Autoclavable Addition Polyimides for 371 °C Composite Applications

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## AUTOCLAVABLE ADDITION POLYIMIDES FOR 371 °C COMPOSITE APPLICATIONS

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### SUMMARY

Studies were conducted to improve the thermo-oxidative stability (TOS) of PMR type polyimides by the substitution of para-aminostyrene (PAS) for the nadic ester endcap in second generation in PMR polyimides (PMR-II). The nadic endcap which provides the PMR polyimides with their relative ease of fabrication, both by limiting the molecular weight of the prepolymer and by undergoing the final addition cure without volatiles, is also the weak link with regard to TOS. A polyimide formulated with PAS endcaps, called V-CAP, utilizes a two step reaction sequence similar to that of the PMR polyimides and can be easily autoclave molded into low void composite materials. Resin studies included two formulations of both PMR-II and V-CAP, corresponding to  $n = 9$  and  $n = 14$  prepolymer stoichiometry. Unidirectional reinforced T40R graphite fiber laminates were fabricated from each of the resins utilizing a vacuum bag molding process and 200 psi pressure. One laminate from each resin was post-cured in either air at 385 °C or nitrogen at 400 °C. Composite specimens were aged in air at 371 °C and mechanical properties were measured at 371 °C before and after exposure.

### INTRODUCTION

In order to keep up with increasing material demands of advanced aeropropulsion systems, the NASA Lewis Research Center has been involved in a long term on-going program to develop high temperature resistance matrix resins for aircraft engine applications. Early studies at NASA Lewis led to the development of the PMR-15 polyimides (ref. 1). Further studies led to the development of second generation PMR (PMR-II) (ref. 2). Both the PMR-15 and PMR-II resins offered excellent processability and thermo-oxidative stability (TOS) at use temperatures as high as 316 °C. More recently, high molecular weight formulations (HMW) of the PMR-II resin were introduced which provided improved TOS at use temperatures as high as 371 °C (ref 3). The HMW-PMR-II resins are autoclavable and exhibit good retention of 371 °C mechanical properties during continuous 371 °C air exposure for 500 hr or more. It is widely recognized that the nadic endcap which gives PMR polyimides their relative ease of fabrication both by limiting the molecular weight of the prepolymer and by undergoing the final addition cure without generating volatiles, is also the weak link with regard to the TOS of the resin. More recent studies to improve TOS of PMR type resins have centered on replacing the nadic endcap with a more thermally stable reactive endcap.

One reactive endcap which offers significant potential for improving the TOS of addition curing polyimides is para-aminostyrene (PAS). An addition curing PMR type polyimide formulated with PAS, labeled V-CAP (Vinyl Capped Addition Polyimide) utilizes a two-step reaction sequence similar to the PMR polyimides.

PAS was initially studied in the 1970's as a lower temperature curing endcap for PMR resins (ref. 4). But recent studies have shown that by using PAS as the endcap in higher molecular weight resin formulations and employing higher cure temperatures, composite TOS could be significantly improved. And so the purpose of this investigation was to determine the effects of substituting PAS for nadic ester on laminate processability, TOS and 371 °C long term mechanical properties. In addition, the effects of air and nitrogen postcuring on laminate properties are also discussed.

## EXPERIMENTAL PROCEDURE

### Resin Preparation

The monomer reactants used to prepare the resins investigated in this study are shown in table I. All the monomers were obtained from commercial suppliers except for the dimethylester (HFDE). HFDE was prepared as a 50 wt % methanol solution by refluxing a suspension of 4,4'-(hexafluoroisopropylidene) 3-bis(phthalic anhydride) (HFDA) until all solids has dissolved, and then continuing for an additional 2 hours. PMR-II and V-CAP reactant solutions were prepared at room temperature by dissolving the reactants in anhydrous methanol to form 40 to 50 wt % solids solutions. The stoichiometric ratio of the monomers used for PMR-II resins containing NE as the endcap was  $n$  moles of the dimethylester (HFDE),  $n+1$  moles of para-phenylenediamine (PPDA), and 2 moles of the monomethylester of 5-norbornene-2,-3-dicarboxylic acid (NE). The ratios of the reactants used to prepare V-CAP resin are:  $n+1$  moles of HFDE,  $n$  moles of PPDA, and 2 moles of the endcap para-aminostyrene. Solutions were prepared at  $n$  values of 9 and 14 for both resin systems.

### Laminate Preparation

All laminates were prepared from unidirectional T40R graphite reinforced prepreg tape. Prepreg tapes were prepared by brush application of resin solutions onto drum wood fiber calculated to yield laminates having 55 vol % fiber after curing. The prepreg was allowed to dry on the drum, under quartz lamps, to a volatile content of 11 to 12 wt %. The prepreg was then removed from the drum and cut into 7.62 cm  $\times$  20.32 plies and a number of plies was stacked unidirectionally to yield laminates having a cured thickness of 0.23 to 0.25 cm. Autoclave cured laminates were then fabricated using the vacuum bag lay-up shown in figure 1. The laminates were cured in a platen press, using a simulated autoclave process, according to the cure schedule shown in figure 2.

After curing, the laminates were given a free standing postcure in either an air or nitrogen gas circulating oven programmed to heat at 20 °C/min to 260 °C and then 1 °C/min to 385 °C with 2 hr holds at 316 and 343 °C, followed by a 20 hr hold at 385 °C for the air post-cured samples. For nitrogen post-cured laminates, the final temperature was 399 °C for 20 hr.

### Laminate Evaluation

Prior to testing, all laminates were inspected for porosity using either ultrasonic C-scan inspection or photomicrographs of laminate cross sections. Flexural and interlaminar shear strength (ILSS) tests were performed on specimens before and after exposure to 371 °C air. Flexural tests were performed

on 0.635 cm wide specimens in accordance to ASTM D-790 at span to depth ratios ranging 24 to 27. ILSS tests were performed on 0.635 cm wide specimens in accordance with ASTM D-2344 at a span/depth of five. Elevated temperature tests were performed in an environmental heating chamber. Property values reported are averages of three to six tests.

Isothermal weight loss measurements were performed on 2.54 by 7.62 cm laminate specimens after exposure to 371 °C air at 1 atm. The air change rate employed was 100 cm/min.

## RESULTS AND DISCUSSIONS

### Laminate Processing

Table I lists the reactants used to prepare the PMR-II and V-CAP resins used in this study. Both resins contain HFDE and PPDA reactants to form the extended chain polyimide backbone of each resin, but employ different endcaps. PMR-II resins are prepared from NE, HFDE and PPDA using a reactant stoichiometric molar ratio of 2 (NE):  $n$ (HFDE)  $n+1$ (PPDA). Whereas V-CAP resins are prepared using PAS as the endcap and has a molar ratio of 2(PAS):  $n+1$ (HFDE):  $n$ (PPDA). For this study, two resin formulations of both PMR-II and V-CAP, corresponding to  $n = 9$  and  $n = 4$  were investigated.

In the earlier studies (ref. 4) to evaluate PAS as a lower temperature curing reactive endcap for PMR type polyimide resins, low molecular weight formulations (LMW) were investigated. During those studies it was found that PAS started to react during the early stages of imidization (~52 °C). This is a problem because the high concentration of endcap in LMW formulations has a significant effect on the processability of PMR type resins. For this study, it was felt that the more oxidation resistant HMW formulations would present fewer processing problems due to the low concentration of endcap present.

To establish the processability of HMW V-CAP resin composites, a series of flat laminates were prepared using the same bagging procedure and cure schedule employed for HMW PMR-II resin composites (ref. 3), as shown in figures 1 and 2, with the exception of the final cure temperature. Figure 3 shows the 371 °C air exposure weight loss characteristics of composites prepared from V-CAP-50 ( $n = 9$ ) resin. It can be seen that the final cure temperature had a significant effect on the 371 °C air oxidation resistance of V-CAP-50 composites. Based on these results, the rest of the laminates investigated in this study were fabricated according to the cure schedule previously established for HMW PMR-II resin composite materials.

Composites were prepared using PMR-II-50 ( $n = 9$ ), PMR-II-75 ( $n = 14$ ), V-CAP-50 ( $n = 9$ ) and V-CAP-75 ( $n = 14$ ). After curing the laminates were post-cured in either air or nitrogen according to the schedule previously described.

### Laminate Evaluation

Figure 4 compares the weight loss characteristics, after 371 °C air exposure, of air and nitrogen postcured laminates prepared using  $n=9$  formulations of PMR-II and V-CAP resins. Weight loss of a Celion 6000 fiber PMR-15 laminate

is also shown for comparison. It can be seen that V-CAP-50 and PMR-II-50 laminates exhibit comparable weight loss at 400 hr exposure. Beyond 400 hr, the V-CAP laminate is significantly lower in weight loss. After 600 hr exposure, the weight loss of the V-CAP laminate is 50 percent lower than the PMR-II laminate postcured in nitrogen. Nitrogen postcuring appears to have a negative effect on the 371 °C TOS of both PMR-II and V-CAP n = 9 formulations.

Figure 5 compares the 371 °C flexural strength retention of V-CAP-50 and PMR-II-50 laminates as a function of 371 °C air exposure. The effect of nitrogen postcuring is evident when comparing the initial 371 °C strengths of laminates prepared from both resin systems. The more than doubling of initial 371 °C flexural strengths result from the increases in glass transition temperature ( $T_g$ ) of the laminates after the nitrogen postcuring. Air postcured laminates exhibited  $T_g$  values of 400 °C for PMR-II and 388 °C for V-CAP n = 9 formulations. Although the V-CAP laminates exhibit lower overall 371 °C flexural strength, they show good retention of strength throughout the exposure time. The lower values for V-CAP laminates is probably due to the aromatic structure of the endcap providing fewer crosslinking sites. However, the aromatic endcap does provide improved TOS over the aliphatic endcap (NE) used in the PMR-II systems. The shorter cut-off in exposure time for PMR-II laminates was due to loose fiber formation on the exposed sample prior to cutting mechanical test specimens.

Figure 6 compares PMR-II-50 and V-CAP-50 371 °C interlaminar shear strength (ILSS) retention after exposure to 371 °C. Retention of ILSS for these laminates are similar to the results shown for 371 °C flexural strength retention in figure 5. Nitrogen postcuring appears to have little effect on V-CAP-50 ILSS properties.

Figure 7 compares the weight loss characteristics of PMR-II-75 and V-CAP-75 (n = 14 resin formulations), air and nitrogen postcured, laminates as a function of exposure to air at 371 °C. The figure shows nitrogen postcuring has a pronounced effect on the TOS of laminates prepared from the n = 14 formulations. Those n = 14 resin laminates exposed to air postcures exhibit TOS comparable to n = 9 laminates during 371 °C exposure as shown in figure 4. The improved TOS of n = 14 resin laminates may be the result of increased or more complete curing of the higher molecular weight resins under nitrogen at 400 °C, whereas the n = 9 resins reach a higher degree of cure during the initial cure at 371 °C. The nitrogen postcured V-CAP-75 laminate exhibits significantly improved 371 °C TOS compared to n = 9 resin laminates and PMR-II-75 laminates, 3 percent at 500 hr versus 5 to 12 percent, for the other formulations. Also, the V-CAP-75 laminate exhibited only 12 percent weight loss after 1000 hr of 371 °C air exposure.

The 371 °C flexural and ILSS retention of the laminates prepared from n = 14 resins and exposed to 371 °C air are in figures 8 and 9, respectively. The 371 °C flexural strength values displayed in figure 8 show that the post-cure environment had little effect on flexural properties of the n = 14 resin formulations. The figure also shows that the V-CAP-75 exhibits excellent strength retention after 1000 hr of exposure to 371 °C air. The low initial strength of the laminate is due to the reduced crosslink density of the n = 14 resin laminates which exhibit  $T_g$ 's values 20 °C lower than those reported earlier for n = 9 resin laminates.

Based on the results shown so far, the data indicates that the V-CAP laminates provide improved TOS over PMR-II laminates prepared from the n = 9 and n = 14 resins. Nitrogen postcuring has little effect on the TOS of n = 9 laminates, but significantly improves the TOS of n = 14 resin laminates.

The results shown for ILSS retention in figure 9 are similar to the 371 °C flexural strength retention. Again, the ILSS values are lower than shown for n = 9 laminates.

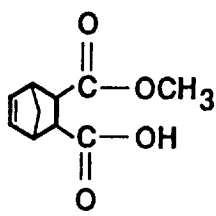
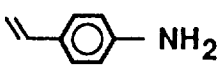
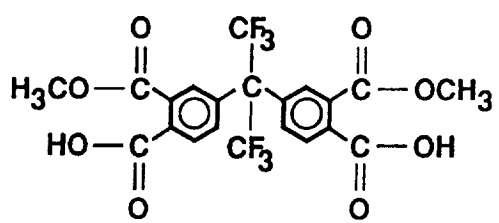
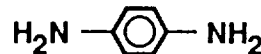
## CONCLUSIONS

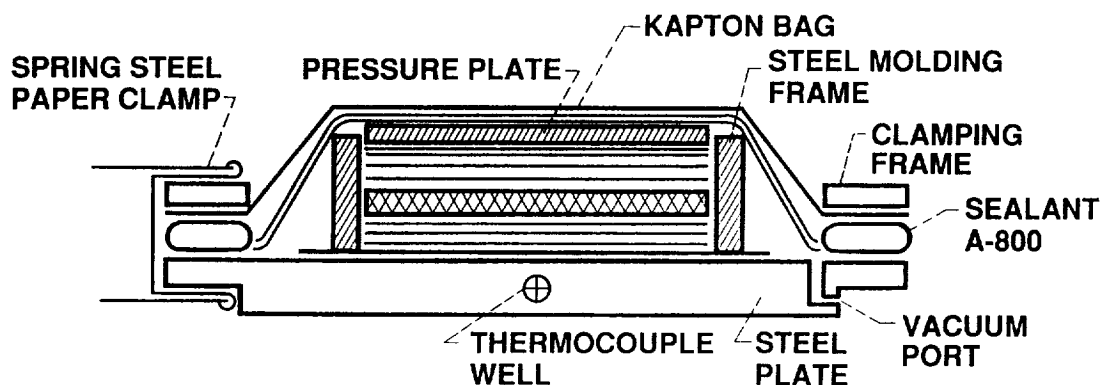
1. The use of para-aminostyrene as an endcap in high molecular weight PMR-II type resins (V-CAP resins) significantly improves TOS.
2. Nitrogen postcuring can provide significantly improved TOS for high molecular weight PMR-II type laminate materials.
3. Nitrogen postcuring provides higher  $T_g$  values for high molecular weight PMR-II type resin laminates than can be achieved with air postcures.
4. Laminates prepared V-CAP-75 resin on T40R fiber exhibit excellent weight and mechanical properties retention out to 1000 hr exposure to air at 371 °C.

## REFERENCES

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2. T.T. Serafini, R.D. Vannucci, and W.B. Alston, "Second Generation PMR Polyimides," Presented at the 21st National SAMPE Symposium and Exhibition, Apr. 1976.
3. R.D. Vannucci and D. Cifani, "700 °F Properties of Autoclaved PMR-II Composites," Proposed for Presentation at the 20th International SAMPE Tech. Conf., Sept. 1988.
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Table I.—Monomers used for resin synthesis.

	MONOMETHYLESTER OF 5-NORBORNENE-2, 3- DICARBOXYLIC ACID	NE
	PARA-AMINOSTYRENE	PAS
	DIMETHYLESTER OF 4, 4'- (HEXAFLUOROISOPROPYLIDENE) - BIS (PHTHALIC ACID)	HFDE
	PARA-PHENYLENEDIAMINE	PPDA



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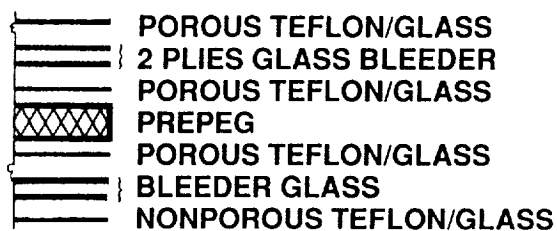


Figure 1.—Vacuum bag system used for autoclave fabrication of PMR-II and V-cap laminates.



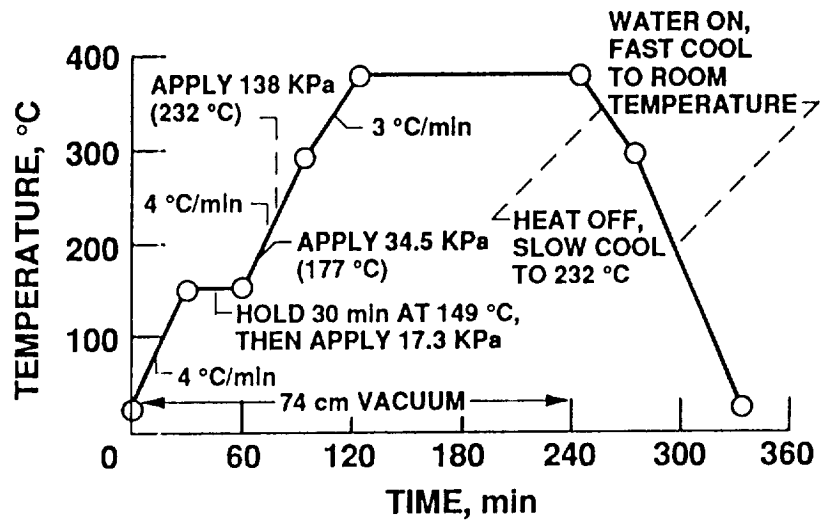


Figure 2.—Autoclave cure cycle for PMR-II and V-cap laminates.

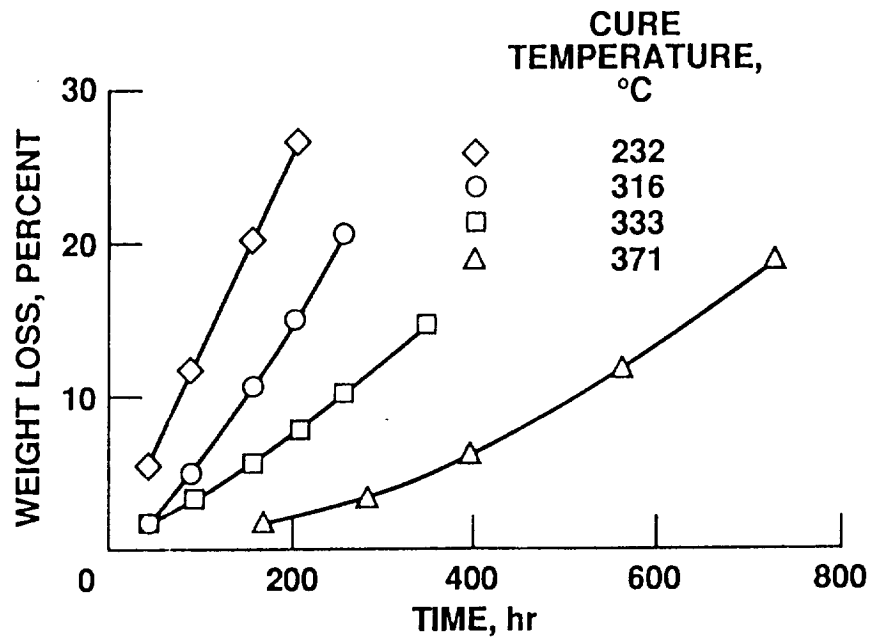


Figure 3.—Weight loss of V-cap-50 laminates as a function of cure temperature after exposure of laminates to air at 371 °C.

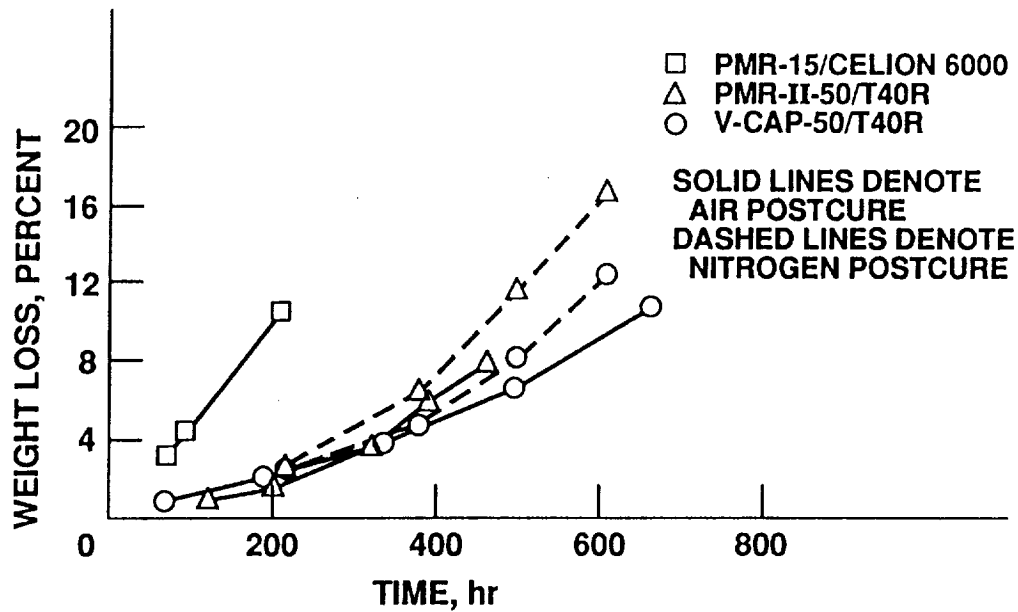


Figure 4.—Weight loss of n = 9 laminates after exposure to air at 371 °C.

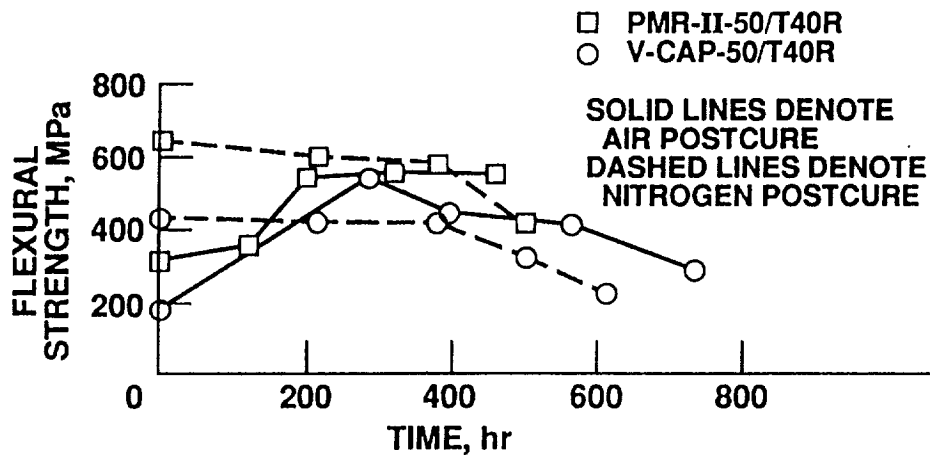


Figure 5.—371 °C flexural properties of PMR-II-50 and V-cap-50 laminates after exposure to 371 °C air.

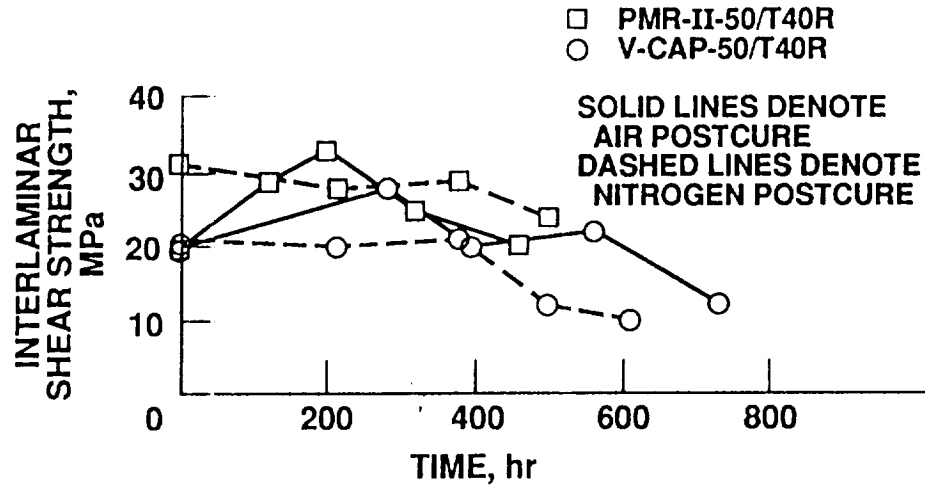


Figure 6.—371 °C interlaminar shear properties of PMR-II-50 and V-cap-50 laminates after exposure to 371 °C air.

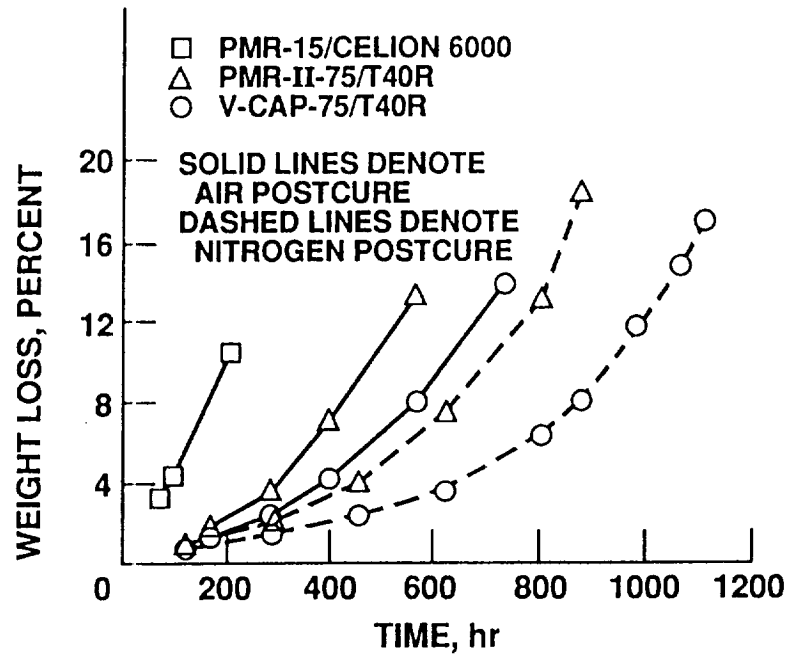


Figure 7.—Weight loss of n = 14 laminates after exposure to air at 371 °C.

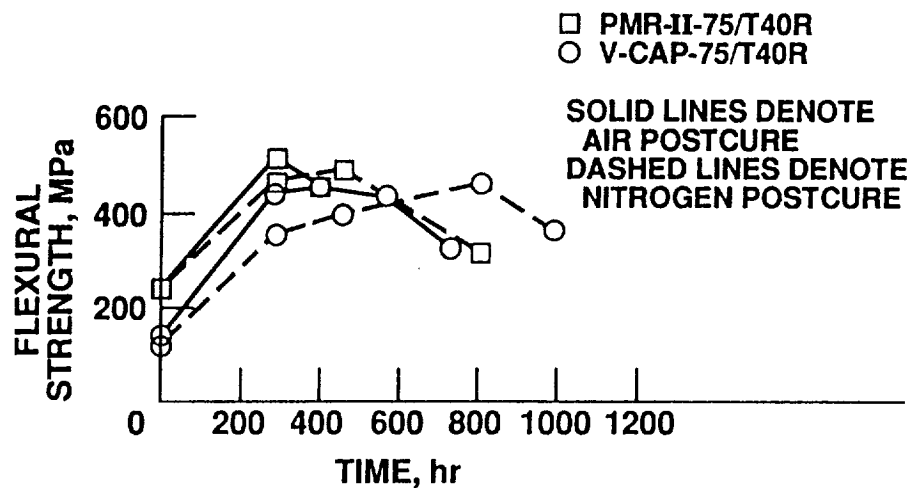


Figure 8.—371 °C flexural properties of PMR-II-75 and V-cap-75 laminates after exposure to 371°C air.

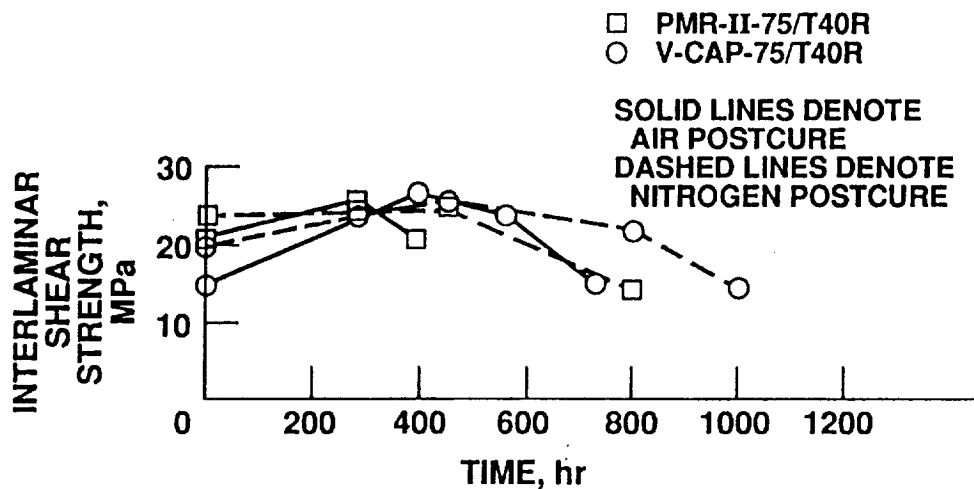


Figure 9.—371 °C interlaminar shear properties of PMR-II-75 and V-cap-75 laminates after exposure to 371 °C air.

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